

## Experiment #2

### Investigating Factors that Affect the Rate of a Chemical Reaction

#### Objective

To experimentally determine the rate equation for the reaction between acetone and iodine in the presence of catalytic hydronium ion. This will be accomplished by investigating the effects of reactant concentrations on the reaction rate.

#### Introduction

Chemical kinetics is the study of the rates at which chemical reactions occur under varying reaction conditions. Each chemical reaction, under specific reaction conditions, proceeds at a characteristic speed called the rate. Reaction rate is defined as the increase in molar concentration of a reaction product per unit time or as a decrease in the molar concentration of a reactant per unit time (see Equation 2). The rates of chemical reactions vary considerably depending on the reaction conditions and on the nature of the reactants and products. Some reactions may reach completion in fractions of seconds while others may take much longer. For example, the reaction of aqueous hydrochloric acid with aqueous sodium hydroxide to produce water and sodium chloride happens almost immediately. On the other hand, the chemical reactions that occur as cement hardens to concrete require years to reach completion.

For the reaction of hydrogen with iodine to form hydrogen iodide,



the reaction rate can be expressed as:

$$\text{rate} = \frac{1}{2}\Delta[\text{HI}]/\Delta t = -\Delta[\text{I}_2]/\Delta t = -\Delta[\text{H}_2]/\Delta t \quad \text{Equation 2}$$

In this equation, the Greek letter delta ( $\Delta$ ) means “a change in.” So equation 1 could be read, the reaction rate equals the change (increase) in molar concentration of HI divided by the change in time. Note that as the concentration of HI increases the concentrations of  $\text{H}_2$  and  $\text{I}_2$  decrease. Thus in Equation 2, the sign is negative for reactants and positive for products so that the reaction rates will always have a positive value. Note also that according to the balanced equation, the rate of increase in HI concentration is equal to one half the rate of decomposition of  $\text{I}_2$  or  $\text{H}_2$ . In other words, in order to equate the rate of reactant decrease with the rate of product increase as shown in Equation 2, it is necessary to divide each equation by the corresponding coefficient from the balanced chemical equation.

Reaction rates are highly dependent on various factors such as concentration of the reactants, reaction temperature, pressures of gaseous reactants and products, presence of catalysts, and even on the nature of the reaction. The usual unit of reaction rate is moles per liter per second or molar per second. For this experiment we will study the effects of reactant concentrations and catalysts on reaction rates. The effects of temperature on reaction rates will be studied in the next unit.

The study of the reaction kinetics has important applications. For example, one can speed up or slow down a chemical reaction in order to control the reaction. Thus, knowledge of reaction kinetics finds practical application in the process of designing chemical technologies and manufacturing processes. Some reactions, under normal conditions, proceed at much too high a rate to be useful for industry until they are moderated (or slowed down). Some are too slow, and as such, may not be profitable in

industrial processes. Once factors controlling the rates of reactions are understood and implemented, industry may find a reaction economical to utilize in their manufacturing technology.

### **Rate Equation**

The rate of a chemical reaction can be expressed as a function of the concentration of the reactants and catalysts as described by the rate law. For example, consider a reaction between reagents A and B in the presence of catalyst C, proceeding according to the following equation:



The rate law for this reaction will look like this:

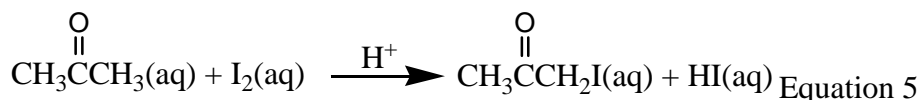
$$\text{rate} = k[A]^x [B]^y [C]^z \quad \text{Equation 4}$$

where k is the rate constant, a proportionality constant characteristic of the reaction at a specific temperature. [A] and [B] are the molar concentrations of the two reactants and [C] is the molar concentration of the catalyst. Exponent x is the reaction order with respect to A, exponent y is the reaction order with respect to B, and exponent z is the reaction order with respect to the catalyst. As can be seen in equation 4, the reaction order for any reactant equals the exponent of the concentration of that reactant in the experimentally determined rate law (x, y, or z in equation 4). The reaction order is often an integer but can also be a fraction or zero. The overall reaction order is the sum of the reaction orders of the individual reactants. For equation 4, therefore, the reaction order equals x + y + z.

A rate equation can only be determined experimentally. To derive it one must continuously chart the changes in the concentration of the reactant(s) or product(s) over time, and then average that change. It can be a tedious process but can be simplified using the method of initial rates. In this method the scientist measures the amount of time necessary for a low concentration of one of the reactants to be completely used at a constant temperature. Then, in a separate experiment, the concentration of that reactant is varied, typically doubled, and the rate is again measured. This process is repeated until all reactants and catalysts have been examined.

### **About the experiment**

In this experiment the kinetics of the reaction between acetone and iodine will be studied:



The rate equation for this reaction may be written as follows:

$$\text{Rate} = k[\text{acetone}]^x [\text{I}_2]^y [\text{H}^+]^z \quad \text{Equation 6}$$

Because iodine has color (yellow) and can be used to determine the end of reaction, it is used as the limiting reagent. The progress of the reaction is monitored by observing the change of the solution color from yellow to colorless.

The rate equation will be determined based on the method of initial rates, using the initial concentration of iodine in the following equation:

$$\text{Rate} = \Delta[\text{I}_2]/\Delta t = -(0 - \text{initial } [\text{I}_2])/(t - 0) = \text{initial } [\text{I}_2]/t \quad \text{Equation 7}$$

The negative sign in the middle equation indicates simply that there is a decrease in the concentration of iodine from its initial value (at time = 0 seconds) to zero at time t (seconds).

When the concentrations of iodine  $[\text{I}_2]$  and acid  $[\text{H}^+]$  are kept constant, and the concentration of acetone is changed while keeping the temperature constant, the order of the reaction with respect to acetone can be determined. If the concentration of acetone is doubled from trial 1 to trial 2, the rate equations for both runs can be written:

$$\text{Trial 1: } (\text{rate})_1 = k[\text{acetone}]^x[\text{I}_2]^y[\text{H}^+]^z \quad \text{Equation 8}$$

$$\text{Trial 2: } (\text{rate})_2 = k(2[\text{acetone}])^x[\text{I}_2]^y[\text{H}^+]^z \quad \text{Equation 9}$$

When Equation 9 is divided by Equation 8:

$$(\text{rate})_2/(\text{rate})_1 = 2^x \quad \text{Equation 10}$$

If the log of both sides of the resulting equation is taken, the order with respect to acetone can be calculated from:

$$x = [\log (\text{rate } 2/\text{rate } 1)]/\log 2 \quad \text{Equation 11}$$

The reaction order with respect to acid (or iodine) can be found in the same way. The concentration of acid (or iodine) is doubled and the concentrations of the other two reagents are kept constant. Reaction orders are calculated as they were for iodine. Once the reaction orders have been calculated, the rate constant can then be calculated from Equation 6 using the experimentally derived values for the reaction orders. The rate equation can then be written using the experimental values determined for k, x, y and z.

### Procedure

Reagents: 4.0 M aqueous acetone,  $5.0 \times 10^{-3}$  M aqueous iodine, 1.0 M hydrochloric acid, and distilled water.

Equipment: at least 3 medium test tubes (clean and dry), a 5 ml volumetric pipette or a 10 ml graduated cylinder, a thermometer, a sheet of plain white paper for a background, and a stopwatch.

**Table 1**

| Trial number | volume of 4.0 M acetone, ml | volume of distilled water, ml | volume of 1.0 M hydrochloric acid, ml | volume of $5.0 \times 10^{-3}$ M $I_2$ solution, ml |
|--------------|-----------------------------|-------------------------------|---------------------------------------|---|
| 1            | 2.0                         | 4.0                           | 2.0                                   | 2.0   |
| 2            | 4.0                         | 2.0                           | 2.0                                   | 2.0   |
| 3            | 2.0                         | 2.0                           | 4.0                                   | 2.0   |
| 4            | 2.0                         | 2.0                           | 2.0                                   | 4.0   |

Use Table 1 to find the exact volumes of the reagents to be used for each trial.

***Trial 1:***

1. Into a clean and dry test tube, drain the required volume of acetone from the appropriate buret. From the buret labeled HCl, drain the required amount hydrochloric acid into the same test tube. Use a volumetric pipet or a graduated cylinder to add the required volume of distilled water to the mixture in the test tube.
2. Into a second test tube, drain the proper volume of iodine solution from a buret labeled  $I_2$  (or pipet the required volume).
3. Add 10 ml tap water to a third test tube (use graduated cylinder). This is your color reference for the end of the first reaction (as well as a rough volume reference provided that all test tubes are of the same size. This way you will know if you correctly added all reagents to reach the total volume of 10 ml).
4. Pour the contents of the test tube with acetone/acid/water into the test tube with iodine solution. Start the stopwatch when about half of the solution has been added. Be careful not to spill any of the mixture. Stir briefly using a clean and dry stirring rod (remove the stirring rod from the mixture). The reaction mixture will be yellow (color of iodine).
5. Set the test tube in a rack or a beaker with white sheet of paper underneath. Next to the test tube with the reaction mixture, place the tube containing 10 ml of tap water.
6. Watch the contents of the reaction mixture. Stop the stopwatch when the yellow color of the reaction mixture completely disappears (the mixture becomes as colorless as the tap water in the reference test tube, indicating that all of iodine has reacted). Record the time to the nearest second.
7. Use this first reaction mixture for the color/volume reference for future trials. Clean and dry the other two test tubes.
8. Repeat Trial 1 using the same volumes of reagents.

***Trials 2, 3 and 4:***

Repeat steps 1-7 using the volumes of reactants listed in Table 1 for Trial 2, (done twice).

Repeat steps 1-7 using the volumes of reactants listed in Table 1 for Trials 3 and 4, respectively (do each trial twice. Repeat any trial for which any problems are noted).

**Calculations**

You should use a separate sheet of paper for your calculations but all calculation sheets must be legible and must be turned in with your lab write up to receive complete credit.

Note: The initial concentrations of the reactants are not the concentrations listed on the reagent labels (or in Table 1). They must be calculated based on the label concentration, the volume of the reagent used, and the final volume of the reaction mixture in the tube.

1. Calculate the rate for each experimental run using  $\text{rate} = \Delta[I_2]/\Delta t = \text{initial } [I_2]/t$
2. Determine the average rate for each trial.
3. Calculate the reaction orders (see equation 11 above) using the reaction rate ratios for proper trials (e.g. trials 3 and 1 are used for the calculation of the order with respect to hydrochloric acid because in trial 3 the concentration of hydrochloric acid was doubled when compared with trial 1, while the concentrations of the other reactants were kept constant).
4. Calculate the rate constant for each run, then calculate the average rate constant using the values for all experimental runs.
5. Write the rate law for the reaction.

**Discussion**

Write a discussion of your results in which you concisely state the purpose of this lab, briefly describe your methodology, and then summarize your results.

**Prelab**

Name \_\_\_\_\_

1. In a test tube, 2.0 ml of 4.0 M acetone solution was mixed with 2.0 ml of 1.0 M hydrochloric acid and 4.0 ml of distilled water. This mixture was added to another test tube containing 2.0 ml of 0.0050 M iodine.

A. Calculate the final volume of the reaction mixture:

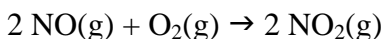
B. Calculate the number of moles of each reagent (acetone, iodine, and acid) in the resulting reaction mixture:

acetone:

iodine:

acid:

2. The rate of the reaction of nitrogen monoxide with oxygen was measured at 25°C starting with various initial concentrations of NO and O<sub>2</sub>.



The data collected is summarized in the following table:

| Trial # | Initial concentration, mol / l |                    | Initial reaction rate, mol / l · s |
|---------|--------------------------------|--------------------|------------------------------------|
|         | NO (g)                         | O <sub>2</sub> (g) |                                    |
| 1       | 0.020                          | 0.010              | 0.028                              |
| 2       | 0.020                          | 0.020              | 0.057                              |
| 3       | 0.040                          | 0.020              | 0.227                              |

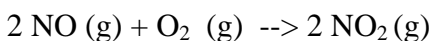
a. Use the method of initial rates to find the reaction orders with respect to NO and O<sub>2</sub>. Hint: for which trials was the concentration of NO changed while [O<sub>2</sub>] remained constant?

**Postlab**

Name \_\_\_\_\_

1. Why was it crucial to use dry test tubes for the kinetic studies of the reaction between acetone and iodine in this experiment? In your answer consider the effect that using moist test tubes would have on the reaction rate. In your explanation, remember to take into consideration all variables involved in the calculation of rate.

2. The rate of the reaction of nitrogen monoxide with oxygen was measured at 25<sup>0</sup>C starting with various initial concentration of reactants NO and O<sub>2</sub>.



The data collected is summarized in the following table:

| Trial# | Initial concentration, mol / l |                    | Reaction rate, mol/l·s |
|--------|--------------------------------|--------------------|------------------------|
|        | NO (g)                         | O <sub>2</sub> (g) |                        |
| 1      | 0.020                          | 0.010              | 0.028                  |
| 2      | 0.020                          | 0.020              | 0.057                  |
| 3      | 0.040                          | 0.020              | 0.227                  |

a. Calculate the rate constant for the reaction (you calculated the reaction orders in the Prelab).

b. Write the complete rate equation using the calculated values for the rate constant and the reaction orders.

c. Calculate the reaction rate for this reaction at 25<sup>0</sup>C, when the initial concentration of NO is 0.010 mol/l and that of O<sub>2</sub> is 0.020 mol/l. Show all calculations involved.